THE EFFECT OF SOME DECOLORIZING AGENTS ON USED CRANK CASE OIL

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The past few years have witnessed a rapid increase in interest in the contamination and dilution of automobile crankcase oils. The present system of changing oil has been compared to a "saving at the spigot, while a leak at the bunghole". It has been estimated that the cars in the United States discard approximately 200,000,000 gallons of oil annually, a waste which for reason of conservation should be checked if possible.

There are various causes of deterioration of automobile crankcase oil in service: The accumulation of solid impurities from dust and sand drawn in through the carburetor, and of metal particles abraided from the bearings in the motor itself: Dilution by the unburnt "heavy ends" of gasoline, or by whole gasoline when starting a cold engine. These cause a lowering of the viscosity of the oil. Another dilution factor is the partial thermal decomposition, or "cracking" of the oil itself due to contact with the hot walls of the cylinders. Conditions existing in the crankcase of a running motor are highly conducive to oxidation. The elements of high temperature, extended surface due to spraying, or exposure in thin films on cylinder walls, and air are all at hand, to say nothing of the possible catalytic action of the metals present. It is known that paraffin hydrocarbons produce many products when oxidized, including water, carbon dioxide, acids from formic up, and anhydrides, lactones,

aldehydes, alcohols, and combinations of these. Waxes and resins are produced upon secondary reactions which give rise to a brown sludge. American lubricating oils are composed chiefly of unsaturated, or cyclic substances. (1) Their reaction to oxidation has been but little studied. It is known that it varies greatly with the brand of oil. The products are similar in character to those of the paraffins.

The characteristic odor of the crankcase oil is largely due to a product of the combustion chamber, where cracking of the heavier fractions of the fuel must occur at times. (Cracking temperatures are not normally reached elsewhere in the engine. (2)) The hydrocarbon responsible can be distilled off at moderate temperatures. The same odor can often be detected in the exhaust.

The various products mentioned above result in a darkening of the color of the oil, and eventually gelatinous sludges more or less soluble in the hot oil, but precipitated on cooling, may be formed. The familiar deep black crankcase oil sludge, does not necessarily consist of, or even contain, these oxidation sludges, which are brown or reddish. The origin of the black sludge like the dilutents, and the odor, is mainly in the combustion chamber and results from imper-

(1) Mobery, "On Viscosity and Lubrication". J. Am. Chem. Soc., 30, 1001 (1908).

(2) Waters, "Some Data on the Oxidation of Automobile Cylinder Oils". Ind. and Eng. Chem., 8, 587 (1916).

fectly burned fuel, or cracked heavy fractions thereof -- soot.(3) This is verified by the fact that when the combustion chambers and exhaust valves of an engine are washed out by kerosene, extremely stable, dense black suspensions of this soot are obtained. Another source is doubtless the insoluble pitches that are formed when some engine oils are strongly evaporated in the air at cylinder surface temperatures in thin films. Also, iron soaps in small amounts are found. This solid matter acts as a stabilizer in oil emulsions.

As ordinarily thought of, crankcase sludge is largely an emulsion of water and oil. In light of the dilution phenomenon it is evident that water, or water vapor, as well as gasoline, gets by the piston rings in large amounts when starting a cold engine, and probably more or less at all times during operation even when the pistons are normally tight. No metal-sealed piston can be gas-tight under the pressures developed in the cylinders. The efficiency of this seal depends to some extent upon the viscosity of the lubricant. When water vapor condenses in contact with oil it forms a fine dispersion, which becomes stabilized by the solid matter in the oil. In cold weather more water vapor is condensed than can be emulsified, because in winter water collects in pools at the bottom of the crankcase. The water can be slowly evaporated out of

(3) Charles van Brunt and P. Schuyler Miller, "Reclamation of Automobile Crankcase Oil". Ind. and Eng. Chem., 17, 416 (1925).

the oil at temperatures below the boiling point, so that the degree of hydration of the sludge may vary in extreme cases to the point of dryness.

In the suspensions mentioned above, the accumulation of organic solids is progressive, very likely autocatalytic so far as concerns the oxidation products. No actual data is at hand concerning the specific effect of these contaminants, unaided by mineral matter, upon the functioning of the oil, yet it is a safe assumption that they are non-lubricants. In the case of the resinification sludges they are probably anti-lubricants through their tendency to form gums and soaps.

Summary of Ways of Reclamation

Many attempts have been made to reclaim or purify crankcase oil. Many patents have been taken out on processes, and more than one device has been patented to attach to the motor of the car to keep the oil efficient.

One of the methods of reclamation is settling. In this process the oil is poured into tanks and heated to the boiling point and held there for twenty minutes and allowed to cool down and then let stand for two weeks. The lightest ends are evaporated off and the water and sediment settle out.

Attempts have been made to centrifuge the oil. But it was found by Flowers, McBerty and Reamer, (4) in 1925, that a

(4) Flowers, McBerty and Reamer, "Reclamation of Used Crankcase Oil". Ind. and Eng. Chem., 17, 483 (1925).

centrifuge was not sufficient to remove the solids from the raw oil.

Filtering by passing the oil under pressure between [illegible] of packed columns of paper has been used to purify the oil. The pressure on the columns regulates the fineness of the particles which pass through. It is possible to filter out colloids in this way.

Many chemical treatments have been tried, such as agitation with solutions of NaOH, Na_2SiO_3, Na_3PO_4, and Na_2CO_3. The chief effect of these compounds is the neutralization of the acids formed when the oil is oxidized.

Experimental

The greatest problem in the recovery of used crankcase oil is to obtain a product which has a good salable color. While color is not a criterion of a good lubricant, the general public is prejudiced toward anything that is "second hand". In order to sell recovered oil it must have as good, or a better color than the new oil. It has been pointed out by Mead that the color change is an index of the amount of oxidation. (5)

The object of this research has been to determine the comparative value of some decolorizing agents upon used oil, the volume of oil that a given weight of Fuller's earth will decolorize efficiently, and the change in the viscosity

(5) Mead; Ind. and Eng. Chem., 19, 1240-6 (1927).

of oil as it runs through the filters of the decolorizing agents.

The oil to be experimented with was taken from used oil that had accumulated at filling stations. It was collected in five-gallon lots. During the first part of this work the oil was agitated with solutions of the various sodium salts named above and solutions of sodium hydroxide. The color of the oil was not affected, in so far as could be detected by the eye.

Aluminum sulphate, alums, and ferrous sulphate were added to the above list, and emulsions were obtained that were slow in breaking up. When they did break the color of the oil remained as before.

Concentrated sulphuric acid was added to the oil with agitation. As a result of this treatment sulphur dioxide was liberated and a black sticky mass settled out of the oil. The oil from this treatment had a much better color. While experimenting with this it was found that when the oil was warmed more sulphur dioxide came off and the residue was slow in settling out of the oil. The sulphuric acid treatment seemed to work better if the temperature was kept below 30° C. and less sulphur dioxide was given off.

Some oil was prepared by blowing air through the oil and adding 20 cc. of concentrated H_2SO_4 per liter of oil. After the acid had all been added the oil was stirred by means of the air stream for one hour. The mixture was allowed to settle for two days. A black gummy mass settled out of the oil

and the oil which was poured off had a good greenish color.

Some of this H_2SO_4-treated oil was washed with a 15% solution of NaOH and then with water. The mixture was allowed to settle another day and the oil was siphoned off the top of the water. Some of this oil was then filtered through an eight-inch bed of Fuller's earth. The oil thus obtained was almost clear and thin when it first began to run out of the filter, but became darker and more viscous as it continued to run.

A filter was made by punching holes in the bottom of a tall can and placing a heavy piece of cloth on the bottom and then a nine-inch layer of Fuller's earth. The drain of the filter was 19 square inches. The weight of Fuller's earth used was four pounds. About every three inches in the Fuller's earth a sheet of parchment was placed. Holes were made in the paper in such a way that the oil could not channel. The level of the oil was kept at about one and one-half inches above the level of the Fuller's earth. The oil began to drip through the filter after eight hours. The oil was collected in 250-cc. samples. These samples came off at the rate of one every four and one-half hours. Five samples were caught from this filter while the level of the oil was kept nearly constant. Then the filter was allowed to almost stop. A day later more oil was poured into the filter, the level being brought back up to one and one-half inches. A total of twelve samples were taken in this run. The last bottle was caught after the filter had started to slow up.

The colors of these samples were determined by a "homemade" colorimeter. It was made by boring one-half inch holes through the sides of a box. The sides were six inches apart. The inside of the box was painted black. Clamps were put on one side to hold test tubes in front of the holes. A slot was made in the side of the box in front of one of the tubes to hold the color glasses. Water was put in one test tube and oil in the other. The color of the oil was determined by adding color glasses until they matched the color of the oil. The source of light was a hundred-watt daylight bulb with a good reflector. It was placed so it would shine through the oil toward the eye.

The samples mentioned above had the following colors:

Sample Number	Red Color Bodies
1	4.5
2	8.0
3	12.5
4	18.0
5	24.0
6	25.0
7	25.0
8	25.0
9	28.0
10	45.0
11	45.0
12	35.0

A comparison run was made using the same oil and the same

weight of Bentonite. (Bentonite is a product of the Tennessee Copper Company. It is an earth which has been chemically treated with the idea of using it as a decolorizing agent for petroleum products.) It was over 48 hours before any oil came through this filter. The oil ran through this one at the rate of one bottle in ten hours. After five samples were caught, the oil being dark, the filter was stopped. The results of the experiment were:

Sample Number	Red Color Bodies
1	8.0
2	20.0
3	27.0
4	30.0
5	50.0

The fifth sample in this run was over twice as red as the corresponding sample on the Fuller's earth run.

Another batch of oil much thinner than the first was run through a new filter of Fuller's earth which was prepared like the first one. This thin oil came through in about three hours and ran at the rate of one bottle every two and one-half hours. The fifth sample on this run was caught at night while the filter was draining. The following are the colors of the light samples caught from this run:

Sample Number	Red Color Bodies
1	7.1
2	10.0
3	13.0

Sample Number	Red Color Bodies
4	12.5
5	14.0
6	15.0
7	17.0
8	21.0

Next an attempt was made to filter this thin oil through a six-inch bed of "Darco". (Darco is an especially-prepared charcoal made by the Darco Sales Corporation, New York City. It can be obtained in granular or powdered form. The powdered form was used in this experiment.) The oil wet the Darco so slowly that none came through during the first week. Then the Darco was wet with oil and it began to filter through very slowly, decolorizing the oil. Only 100 cc. came through this filter in a week. On account of the slow rate of filtering this idea was abandoned.

It was thought that this thin oil came through the Fuller's earth too fast to obtain the best results, so a mixture of 3/4 pound Darco and 3 pounds Fuller's earth was placed in the filter. Samples caught from this filter gave the following colors:

Sample Number	Red Color Bodies
1	5.0
2	5.5
3	8.0
4	12.0
5	13.0

Sample Number	Red Color Bodies
6	25.0
7	26.0
8	27.0
9	30.0

The rate of flow from this filter was about one bottle every six hours.

It was decided to run the viscosities of the samples of oil in the above experiments. First the viscosity was run on the two samples of oil used. The heavy oil in the first two experiments has a viscosity at 100° F. of 531 seconds. The oil used in the third and fourth experiments had a viscosity of 183 seconds. These viscosities were run by means of a Saybolt Universal Viscosimeter.

The following tables give the viscosities of the samples in each experiment:

Experiment 1

Sample Number	Viscosity in Saybolt seconds at 100° F.
1	218.6
2	281.0
3	322.2
4	454.8
5	471.8
6	511.8
7	535.1
8	540.1
9	536.1

Sample Number	Viscosity in Saybolt seconds at 100° F.
10	520.0
11	543.0
12	590.0

Experiment 2

Sample Number	Viscosity in Saybolt seconds at 100° F.
1	221.4
2	266.8
3	298.8
4	322.0
5	330.8

Experiment 3

Sample Number	Viscosity in Saybolt seconds at 100° F.
1	137.2
2	148.6
3	174.0
4	170.0
5	181.0
6	179.0
7	182.4
8	182.0

Experiment 4

Sample Number	Viscosity in Saybolt seconds at 100° F.
1	160.0
2	174.4

Sample Number	Viscosity in Saybolt seconds at 100° F.
3	175.8
4	175.2
5	180.6
6	188.8
7	200.1
8	211.0
9	208.0

Conclusions and Discussion of Results

Sulphuric acid is a very good decolorizing agent, but it is very likely that it removes some of the desirable compounds from the oil, as lubricants consist chiefly of unsaturated compounds. To determine how far it is practical to go with this sulphuric acid treatment would afford a good problem for research.

Fuller's earth seems to be the best decolorizing agent of those considered. The results show that it is far superior to Bentonite, the fifth sample from the Bentonite being over twice as dark as the corresponding sample in the Fuller's earth run.

Approximately three liters of the heavy oil can be decolorized with four pounds of Fuller's earth. The last liter of the oil is too dark, but it could be blended with the first liter which is too light in color and too low in viscosity.

Besides decolorizing the oil, the Fuller's earth has some kind of fractionating effect upon it. This can be seen

by the fact that the viscosity of the first few bottles of the oil was low. It gradually increased until it reached that of the original oil. The heaviest ends of the oil are held longest, as is shown by the viscosity of the sample that drained from the earth when the filter was slowing up.

The "Darco" by itself is not as efficient as the Fuller's earth in decolorizing properties. By the presence of a quarter of a pound of Darco to every pound of Fuller's earth, the decolorizing power of the earth was increased for the first few samples. If the product desired was to be below thirty in red color bodies, the efficiency of the Fuller's earth would be increased about 18% by the presence of Darco in the ratio of one to four. The increased efficiency is probably due to the decrease in the rate of flow through the filter. An interesting problem for research would be the study of the effect of the rate of flow upon the color of the oil. This might be carried out in two ways: by varying the depth of the bed, or by adding some fine substance such as Darco which would increase the resistance to flow. In carrying out such an experiment the head of the oil and the temperature should be kept constant.

The following would be submitted by the author as a process for reclaiming used oil: The oil should be allowed to stand for two or three weeks in settling tanks. During this time the sludges would settle out, and most of the gasoline would evaporate. The oil should then be poured off these residues and treated with sulfuric acid, the quantity of acid should be varied from 15 to 20 cc. per liter, depending upon the color of the oil. The mixture should be well stirred while

adding the acid, and for s short time afterwards. After the oil has separated from the residue formed by the acid it should be poured off and neutralized with a solution of NaOH or lime and washed with water. When the oil and the water have separated the oil should be filtered through a layer of Fuller's earth. In preparing the filter it is advisable to interlay the earth with baffles to prevent channeling and give a longer path of flow.